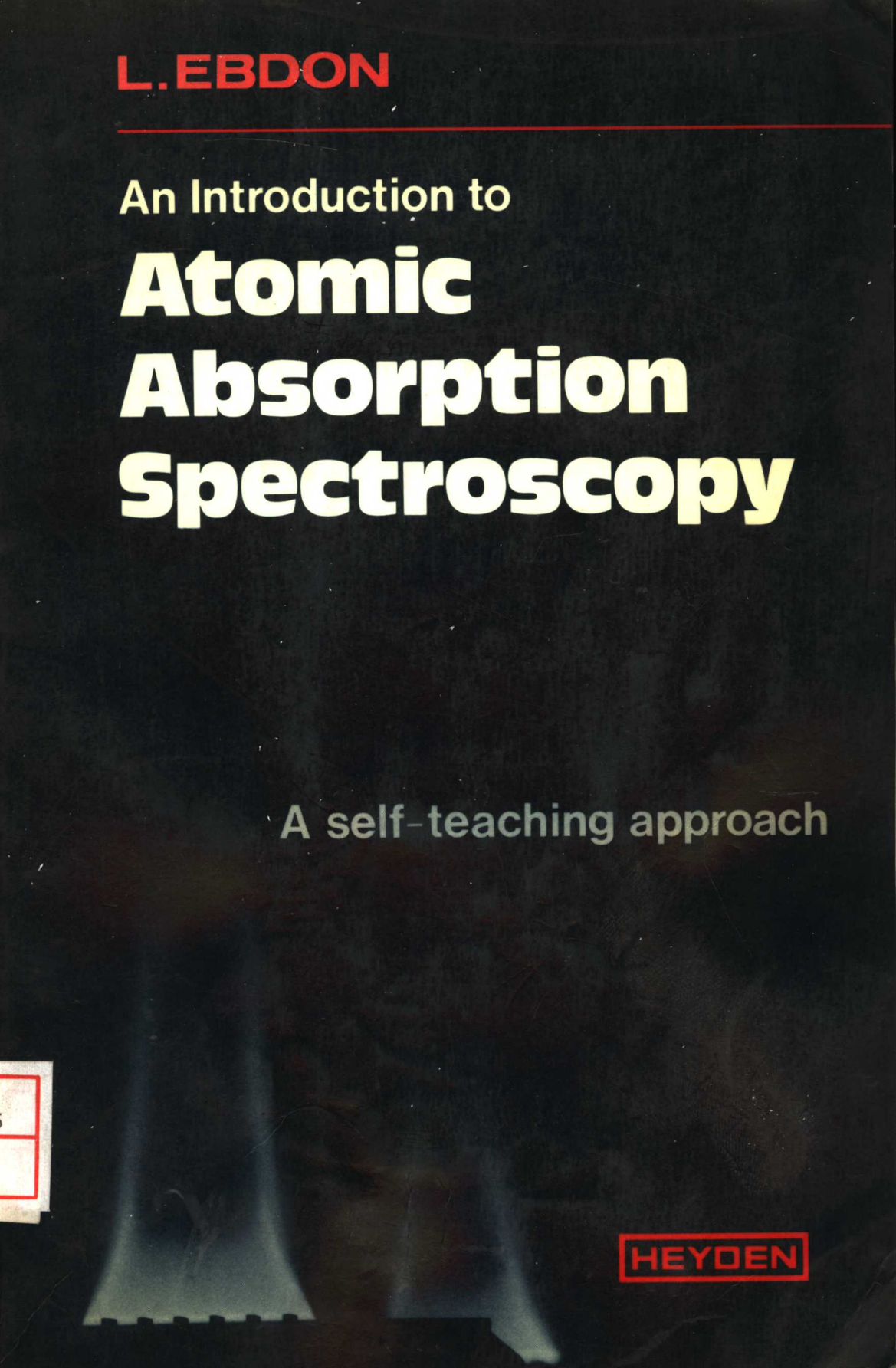
L. EBDON

An Introduction to Atomic Absorption Spectroscopy

A self-teaching approach



HEYDEN

An Introduction to Atomic Absorption Spectroscopy

A Self-teaching Approach

L. Ebdon

Reader in Analytical Chemistry

Plymouth Polytechnic, Devon, UK

HEYDEN

LONDON • PHILADELPHIA • RHEINE

Heyden & Son Ltd, Spectrum House, Hillview Gardens, London NW4 2JQ, UK
Heyden & Son Inc., 247 South 41st Street, Philadelphia, PA 19104, USA
Heyden & Son GmbH, Devesburgstrasse 6, 4440 Rheine, West Germany

British Library Cataloguing in Publication Data

Ebdon, L.
An introduction to atomic absorption spectroscopy.
1. Atomic absorption spectroscopy
I. Title
535.8'4 QC454.A8

ISBN 0-85501-714-7

© Heyden & Son Ltd, 1982

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright holder.

Photoset by Paston Press, Norwich
Printed in Great Britain by Mackays of Chatham Ltd

PREFACE

Atomic absorption spectroscopy offers an excellent example of the need for continuing study and training. No other instrumental analytical technique has ever shown such rapid growth in applications, yet the theory and methodology of atomic absorption are but poorly covered in many basic chemistry courses. It is hard to escape the conclusion that this sad state of affairs arises not only from rapid growth, but also because of a certain unprofessional aloofness on the part of many teachers, possibly affronted at the wide industrial popularity of a technique so elegantly simple and undemanding of spectroscopic theory, and a certain jealously by advocates of superseded analytical techniques.

Rapid technological development and the increasingly volatile nature of employment in the scientific world ensure that few, if any, can expect to leave school or college equipped with a range of skills and learning which will serve all our working life. Indeed, part of the current debate about full-time education is the extent to which vocational studies should appear on the curriculum. We can certainly agree that an aim of such education should be the equipping of students with the abilities necessary for self-teaching after graduation.

Traditionally, those wishing to acquire new knowledge in mid-career or at the start of a new career have turned either to evening classes or correspondence courses. In advanced vocational subjects, the evening class has developed, via day release, into part-time day and evening courses, typified in the UK by several M.Sc. courses in Instrumental Chemical Analysis and many post-HC courses in Advanced Analytical Chemistry (the so-called LRSC courses). The less-generous economic climate now prevailing has placed considerable difficulties in the way of those seeking day release to go on such courses, or attempting to attend more intensive short courses on single techniques. For several years, I was involved in the teaching of atomic absorption spectroscopy on the relatively-successful part-time M.Sc. course in Instrumental Chemical Analysis at Sheffield City Polytechnic. When we came to review the course prior to the periodic resubmission to the Council for National Academic Awards, we considered this dilemma. There was clearly a growing need for the course, yet potential students were finding it increasingly difficult to obtain the necessary half-day release. We were aware that one of the most spectacular educational successes of the past decade has been the Open University. The major features of their

method of study are not the much-publicized televised components, but the books of study material. If this approach could be successful at the undergraduate level, it seemed likely that it should be applicable at the postgraduate level. The decision was taken to teach half the traditional lecture programme by individualized learning methods. This book sprang from that decision. The material which I wrote to teach the part of the syllabus covering atomic absorption, emission and fluorescence spectroscopy in flame and electrothermal atom cells was so well received by the students, that I was encouraged to publish the course for a wider public.

This book, while it is based upon that original self-learning material, has been expanded and amended in several ways. Obviously, I have tried to ensure that the contents have been brought completely up to date, even in those areas where developments are being made rapidly. The book now assumes no advanced prior knowledge and is as self-contained a course as is possible without dilution of the basic aim to teach atomic absorption spectroscopy. An attempt has been made to retain a succinct style of writing with keywords highlighted to aid revision. At the suggestion of the students who found them helpful, I have included more questions and I hope this will aid readers who have to study this book independently.

The contents follow the structure that students have told me is most useful. After a brief historical introduction, common elements of instrumentation are considered, followed by a detailed discussion of the flame as an atom cell. The following chapters consider, in turn, flame emission, flame atomic absorption and flame atomic fluorescence spectroscopy. In view of the very wide interest in it as the technique of choice for trace metal analysis, atomic absorption is dealt with in most detail. In each case, the exposition develops from basic theory, through practical instrumentation to real application. Succeeding chapters deal in depth with practical aspects such as interferences and applications, before attention is directed to the recent, significant growth in the use of atom cells other than flames. The final chapter looks at electrothermal atomization in considerable detail, concluding with a survey of the relative merits of this approach.

I hope that the reader will find this book a real contribution to the literature of analytical chemistry. Several eminent workers in the field have commented to me on the lack of an introductory book suitable for self-teaching the newcomer to atomic absorption spectroscopy. While I should be proud to think that the old 'AA hand' can find something new and of value here, I shall derive most satisfaction from helping the student or analyst who is meeting an atomic absorption spectrometer for the first time. I hope that, like me, they will find this useful technique elegant in its simplicity and versatile in its capability, and come to find the practice of analytical atomic spectroscopy profoundly satisfying.

Les Ebdon
Plymouth
July 1981

此为试读,需要完整PDF请访问: www.ertongbook.com

ACKNOWLEDGEMENTS

I acknowledge with thanks the following for permission to reproduce copyright material: W. J. Price for Fig. 1.7, taken from *Spectrochemical Analysis by Atomic Absorption*, Heyden & Son, London (1979); G. F. Kirkbright, A. Semb, T. S. West and Maxwell Scientific Inc., New York, for Figs 2.9 and 2.10, taken from *Talanta* **14**, 1014 (1967); W. B. Barnett, J. W. Vollmer and S. M. DeNuzzo and the Perkin–Elmer Corporation, Norwalk, Connecticut for Fig. 4.3, taken from *Atomic Absorption Newsletter*, **15**, 33 (1976); H. T. Delves and the Royal Society of Chemistry, London, for Fig. 8.1, taken from the *Analyst* **95**, 431 (1970); B. V. L'vov and Pergamon Press, Oxford, for Fig. 11.1, taken from *Spectrochimica Acta* **24B**, 55 (1969); H. Massman and Pergamon Press, Oxford, for Fig. 11.2, taken from *Spectrochimica Acta* **23B**, 217 (1968); P. J. Whiteside and Pye-Unicam Ltd., for Fig. 11.4.1; C. W. Fuller and the Royal Society of Chemistry, London, for Figs 11.4.2 and 11.4.3, taken from *Electrothermal Atomization for Atomic Absorption Spectrometry*, Chemical Society, London (1977); and K. C. Thompson, D. R. Thomerson and the Royal Society of Chemistry, London, for Table 10.1, which originally appeared in the *Analyst* **99**, 595 (1974).

Figures 2.2 and 2.3 are adapted from Lewis and Van Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press, New York (1961). Thanks are also due to Pye–Unicam Ltd., Instrumentation Laboratory, and Varian Techtron, from whose sales literature Figs 4.1, 4.8 and Table 7.1, respectively, are taken or adapted.

Thanks are also due to all those who have encouraged me in this undertaking, particulary those students who first recommended publication and those, including my research students, who made helpful comments on presentation. I am grateful for the support of former colleagues at Sheffield City Polytechnic, especially Dr. M. Goldstein, Head of Chemistry, for first suggesting that my lecture material might be presented in this way. No author should omit mention of the inspiration he has received from his own teachers. In my case, mention must be made of Professor G. F. Kirkbright and Professor T. S. West.

Finally, my largest debt is to my family for their forbearance during the preparation of this book, most notably my wife Judith who typed the original manuscript and its many drafts.

AIMS

To introduce and develop a knowledge of the theory, instrumentation and practice of atomic absorption, emission and fluorescence spectroscopy in flame and electrothermal atom cells.

To discuss the applications of these techniques to a range of typical problems in analytical chemistry.

To compare the relative merits of the above techniques in analytical situations.

To introduce an understanding of currently developing themes in the field and enable the student to follow current advances through the means of the scientific literature.

To enable the student to develop and use precise and accurate analytical methods for a range of determinations using the above techniques.

PRIOR KNOWLEDGE

An attempt is made in this book to approach analytical atomic spectroscopy without requiring extensive prior knowledge. An understanding of the structure of the atom and basic spectroscopy is required, but this is not assumed to be at graduate level; for most of the book, an understanding at the level of the Bohr theory will suffice. It is assumed that some basic instrumentation is known, and no detailed discussion of optical or standard electrical components is given.

INTRODUCTION AND SUGGESTED STUDY TIME-TABLE

The learning material is designed to replace traditional learning systems, such as lectures, as adequately as possible. While therefore it covers a definable 'course' it is, like lectures, designed to be read in conjunction with supplementary texts. Background reading in the original and current literature is very valuable.

By setting aside an evening a week for study, the reader may complete this book in five weeks. A suggested study time-table is given below.

Week 1	Chapters 1 and 2
Week 2	Chapters 3, 4 and 5
Week 3	Chapters 6 and 7
Week 4	Chapters 8, 9 and 10
Week 5	Chapter 11

Questions are interspersed with the material. You should satisfy yourself that you can answer a question from the material above it before proceeding.

CONTENTS

PREFACE ix
ACKNOWLEDGEMENTS xi
Aims xiii
Prior Knowledge xiii
Introduction and Study Time-table xiii

1 INTRODUCTION 1
1.1 Historical 1
1.2 Basic Instrumentation 3
1.3 Optics for Spectrometers 4
1.4 Detectors 8

2 FLAME SPECTROSCOPY 11
2.1 Flame Structure 11
2.2 Flame Temperatures 12
2.3 Flame Gas Mixtures 14
2.4 Sample Introduction and Sample Atomization 16
2.5 Burner Design 20
2.6 Flame Spectra 22
2.7 Broadening 24

3 FLAME EMISSION SPECTROSCOPY 27
3.1 Theory 27
3.2 Instrumentation 29
3.3 Other Sources for Atomic Emission Spectroscopy 32
3.3.1 Introduction 32
3.3.2 Solid sampling emission sources 34
3.3.3 Plasma sources 36

4 FLAME ATOMIC ABSORPTION SPECTROSCOPY 42
4.1 Theory 42
4.2 Instrumentation 45
4.2.1 Sources 45

4.2.2 The most popular atom cells: flames 48
4.2.3 Instrument design 49
4.2.4 Read-out systems 55
4.2.5 Sensitivity and limit of detection 56

5 FLAME ATOMIC FLUORESCENCE SPECTROSCOPY . . . 58
5.1 Theory 58
5.2 Instrumentation 59
5.2.1 Sources 59
5.2.2 Flames 61
5.2.3 Instrument design 62

6 INTERFERENCES AND ERRORS IN FLAME SPECTROSCOPY 63
6.1 Sample Pre-treatment Errors 63
6.2 Operator Errors 64
6.3 Instrument Errors 65
6.4 Interferences 66
6.4.1 Spectral interferences 66
6.4.2 Ionization interferences 67
6.4.3 Chemical interferences 67

7 THE PRACTICE OF FLAME SPECTROSCOPY 71
7.1 Applications 73
7.1.1 Clinical, food and organic samples 73
7.1.2 Agricultural samples 73
7.1.3 Water and effluents 75
7.1.4 Geochemical and mineralogical samples 75
7.1.5 Metals 76
7.1.6 Solvent extraction of trace metals 76
7.2 Comparison of the Analytical Utility of Atomic Emission Spectroscopy, Atomic Absorption Spectroscopy and Atomic Fluorescence Spectroscopy 77

8 MODIFICATIONS TO FLAME SPECTROSCOPY 80
8.1 The Limitations of Conventional Flame Cells 80
8.2 Modified Flame Cells 81
8.2.1 Pulse nebulization 81
8.2.2 Branched uptake capillaries 81
8.2.3 Kahn sampling boat 82
8.2.4 Delves sampling cup 82
8.3 Further Arguments about Flame Atom Cells 83

9 MERCURY DETERMINATION 86
9.1 The Reduction–Aeration Method 86
9.2 Cold-vapour Atomic Absorption Spectroscopy 87
9.3 Cold-vapour Atomic Fluorescence Spectroscopy 88

10 HYDRIDE GENERATION 90
10.1 Chemistry 90
10.2 Instrumentation 91

11 ELECTROTHERMAL ATOMIZATION 92
11.1 Historical Development 92
11.2 Heated Graphite Furnace Atomizers 95
11.3 Filament and Mini-Furnace Graphite Atomizers 98
11.4 Recent Developments in Electrothermal Atomizer Designs 99
11.4.1 Control of furnace temperature 99
11.4.2 Tube dimensions 100
11.4.3 Isothermal operation 100
11.5 Atomization Mechanisms 101
11.5.1 Thermodynamic considerations 101
11.5.2 Kinetic considerations 102
11.6 Interferences 103
11.6.1 Physical interferences 103
11.6.2 Background absorption 104
11.6.3 Memory effects 104
11.6.4 Chemical interferences 104
11.7 Applications 106
11.8 The Relative Merits of Electrothermal Atomization 107
11.8.1 Advantages of electrothermal atomization 107
11.8.2 Disadvantages of electrothermal atomization . . . 109

APPENDICES 110
Appendix A: Revision Questions 110
Appendix B: Practical Exercises 114
Calculations 114
Safety procedures 117
Experiments 119
Appendix C: References and Bibliography 130

INDEX 134

1 INTRODUCTION

1.1 HISTORICAL

Spectroscopy is generally considered to have started in 1666, with **Newton's** discovery of the solar spectrum. **Wollaston** repeated Newton's experiment and in 1802 reported that the sun's spectrum was intersected by a number of dark lines. **Fraunhofer** investigated these lines—Fraunhofer lines—further, and in 1823 was able to measure their wavelengths.

Early workers had noted the colours imparted to diffusion flames of alcohol by metallic salts, but detailed study of these colours awaited the development of the premixed air–coal gas flame by **Bunsen**. In 1859, **Kirchhoff** showed that these colours arose from line spectra due to elements and not compounds. He also showed that their wavelengths corresponded to those of the Fraunhofer lines. Kirchhoff and Fraunhofer had been observing atomic emission and atomic absorption, respectively.

Atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and later atomic fluorescence spectroscopy (AFS) then became more associated with an exciting period in astronomy and fundamental atomic physics. Atomic emission spectroscopy (AES) was the first to re-enter the field of analytical chemistry, initially in arc and spark spectrography and then through the work of **Lunegardh**, who in 1928 demonstrated AES in an air–acetylene flame using a pneumatic nebulizer. He applied this system to agricultural analysis.

The term **flame emission spectroscopy** is applied to the measurements of light emitted from flames by chemical species after the absorption of energy as heat or as chemical energy (i.e. chemiluminescence). An older term is **flame photometry**. If only the emission from atoms is observed, the term **atomic emission spectroscopy** is preferred.

Atomic absorption spectroscopy is the term used when the radiation absorbed by atoms is measured. The application of AAS to analytical problems was considerably delayed because of the apparent need for very high resolution to make quantitative measurements. In 1953, **Walsh** brilliantly overcame this obstacle by use of a line source, an idea pursued independently by **Alkemade**, his work being published in 1955.

The re-emission of radiation from atoms which have absorbed light is

此为试读,需要完整PDF请访问: www.ertongbook.com

termed **atomic fluorescence**. In 1962, **Alkemade** was the first to suggest that AFS had analytical potential, which was demonstrated in 1964 by **Winefordner**.

These three types of spectroscopy are summarized diagrammatically in Fig. 1.1.

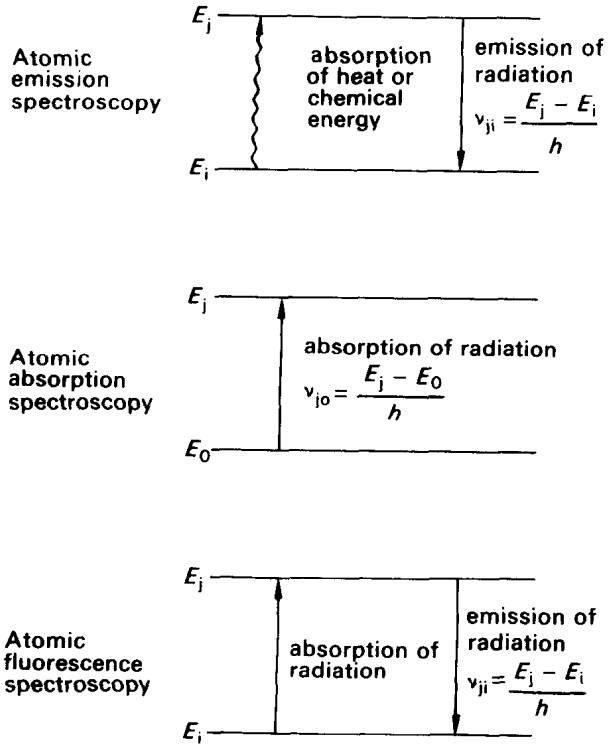


Fig. 1.1 Summary of AES, AAS and AFS.

The horizontal lines represent different energy levels in an atom. E_0 is the term used for the lowest energy level, which is referred to as the **ground state**. In flames, atoms are most commonly encountered in the ground state and therefore all **practical absorption** measurements originate from atoms in the ground state, as do virtually all practical fluorescence measurements. E_i and E_j refer to other energy levels, E_j being higher (greater energy) than E_i. A solid vertical line refers to a **transition** involving the absorption or emission of energy as radiation. The wavy line refers to a **non-radiative transition**. The energy of the radiation absorbed or emitted is quantized according to **Planck's equation**, $E = h\nu$, where h is Planck's constant, ν is the frequency of the radiation and E is the energy difference between the two energy levels in the atom. The frequency is related to **wavelength** by the formula λ (wavelength) = c (speed of light)/ν.

Q. What is the fundamental difference between AES and AFS?

1.2 BASIC INSTRUMENTATION

Figure 1.2 shows the basic instrumentation necessary for each technique. At this stage, we will define the component where the atoms are produced and viewed as the 'atom cell'. Much of what follows will explain what we mean by this term. In atomic emission spectroscopy, the atoms are excited in the atom cell also, but for atomic absorption spectroscopy and atomic fluorescence spectroscopy, an external light source is used to excite the ground state atoms. In atomic absorption spectroscopy, the source is viewed directly and the attenuation of radiation measured. In atomic fluorescence spectroscopy, the source is not viewed directly, but the re-emitted radiation is measured.

Current instrumentation usually uses a **diffraction grating** as the dispersive element and a **photomultiplier** as the detector. Rapid-scanning photoelectric detectors, such as Vidicon tubes, have been used in some research instruments.

A variety of **read-out systems** are in use. These include analogue meters, often with the capability of reading linearly in absorbance, chart recorders, paper tape print-out, digital display and several microprocessor-controlled

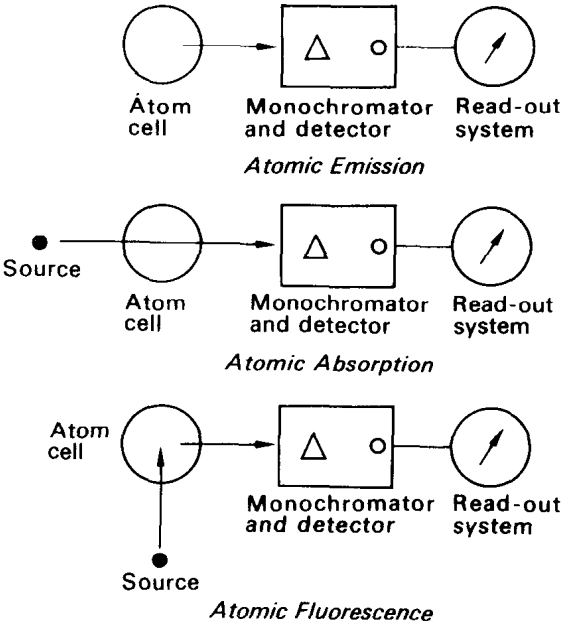


Fig. 1.2 Basic instrumental systems used in analytical atomic spectroscopy.

displays. With the latter, calibrations may be performed automatically, and data on concentration, standard deviation etc. presented on a visual display unit.

As may be seen, most of these components are common to a wide variety of instrumentation, and in the next two sections some typical arrangements will be outlined.

Q. Explain the different geometries used for AAS and AFS.

1.3 OPTICS FOR SPECTROMETERS

To exploit the full potential of atomic spectroscopy, it is usually necessary to isolate a **narrow band of wavelengths**. As will be seen, this is particularly important for atomic absorption spectrometry. This isolation may be achieved by the use of **filters** or by **geometrical dispersion**. Dispersion is generally preferred, although filters may be used in some simple emission instruments.

Coloured glass filters which absorb most radiation, but allow some wavelengths to be transmitted, are widely available. Unfortunately, their **transmission windows** are quite large (e.g. 40 nm), which severely limits their use. Filters which function on the interference principle, i.e. **interference filters**, transmit much smaller bands of wavelength (e.g. 10 nm) and are more useful, but expensive. They can be made by depositing a very thin, **semi-transparent** film of silver on a glass or quartz plate, covering this film with a very thin layer of a **transparent material** such as magnesium fluoride and then with another **semi-transparent layer** of silver. As each silver film reflects about half of the radiation that strikes it, some of the light will be **repeatedly reflected** before it is transmitted. The emergent rays will reinforce each other only for radiation with a wavelength which is an **exact multiple** of twice the distance between the two silver films. For all other radiation, the distance travelled by the light rays in the filter is not an exact multiple of their wavelength, and so the beams interfere destructively. The transmitted radiation is **more intense** than that from a coloured glass filter, but consists of multiple orders. The unwanted orders can be removed by making the base plate, or a cover plate, absorptive in the correct region.

A **monochromator** is an instrument that can isolate a narrow range of wavelengths (e.g. 1–0.01 nm) anywhere in a comparatively **wide spectral range** (for atomic absorption spectroscopy, typically 190–900 nm). The better resolution and the ability to select any desired wavelength make monochromators the preferred means of wavelength isolation for atomic absorption spectrometry.

Although most modern instruments use **replica diffraction gratings** to achieve dispersion, many early instruments used **prism monochromators**. As many of the most analytically useful atomic absorption lines occur in the ultraviolet, prisms made of silica (e.g. fused quartz) were used. The **60° prism** traditionally used in spectrographic instruments can be replaced in a more **compact** and **economical** way by a **30° prism** with its back surface silvered. This so-called **Littrow design** is shown in Fig. 1.3. The passage of radiation through the quartz in both directions will also correct for any **birefringence**. The use of a **concave mirror** rather than a lens to focus the light on the prism and on the **exit slit** enables the coverage of a greater **optical range** and **eliminates chromatic aberration**, a significant problem with lenses.

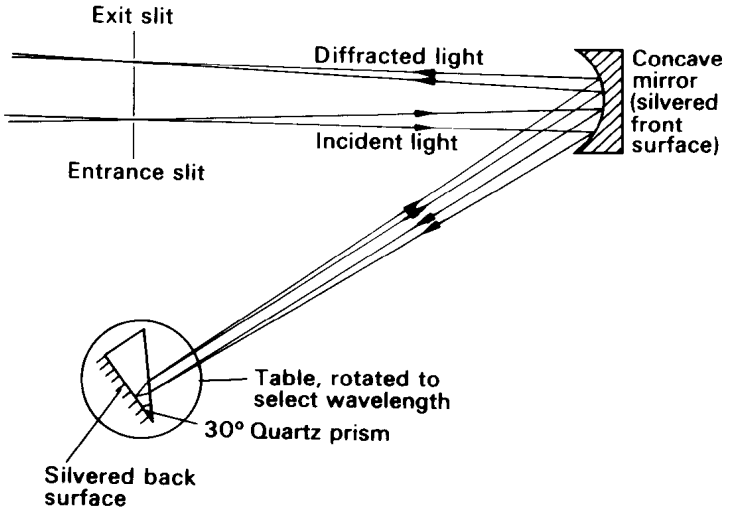


Fig. 1.3 Littrow-mounted prism monochromator.

The **dispersion** given by a prism is high in the ultraviolet, but **decreases** rapidly **as wavelength increases**. **Gratings** give a dispersion which is essentially **constant** throughout the spectrum, depending instead on the number of **rulings** per unit width and the **focal length** of the monochromator. The **energy** transmitted by a prism may be greater, as it is not split into different orders and there are usually few **stray light** or **ghost** problems (faint false lines on each side of the true spectral line). As **gratings** have improved, stray light and ghost problems have been diminished, and **blazing** the grating enables most of the energy to be thrown into the first order. The **cost** of replica gratings now compares favourably with that of prisms. **Holographic gratings**, which can be cut into a photosensitive resin using the interference fringes of two coherent lasers, offer considerable improvements in perfor-

mance, and with modern technology they can also be blazed economically. Hence, the use of gratings is becoming increasingly popular.

The theory of a diffraction grating involves **Huygens' principle** of secondary wavelets and is really beyond our scope. A simplified discussion of arguments for a transmission grating may be helpful; this can easily also be applied to a reflection grating. A **transmission grating** consists of a transparent plate with a great many lines ruled upon it (e.g. 20 000 lines cm^{-1}). These act like regularly spaced narrow slits. From these, the light will emerge as a series of intersecting wavelets like a series of **semi-circles** emanating from **each slit**, i.e. as if each slit were itself a source of radiation. In a short time, the wave systems will recombine to form the original wavefront, the so-called **zero-order**. More interestingly, at a **series of angles**, θ, to the grating, there will be **constructive interference** for light of a given wavelength. The position of these diffraction wavefronts is given by the **grating equation**:

$$n\lambda = d \sin \theta$$

where λ is the wavelength, d is the space between the rulings on the grating, and n is an integer (0, 1, 2, 3 . . .) called the **order**. Thus, a beam of polychromatic radiation is diffracted into a series of spectra symmetrically located on either side of the normal to the grating. It should be noted that for any given θ there will be several different wavelengths, albeit in different orders. This **overlapping** problem is reduced by **blazing** the grating to a level which generally gives rise to no problems, and may be eliminated by the use of filters or a preliminary **order sorting** prism.

Figure 1.4 shows schematically a **blazed reflection grating**. A ray incident at an angle α will be reflected from the groove face at an angle β, such that $\alpha + \phi = \beta - \phi$, where ϕ is the **angle of blaze**. Such a grating, also known as an echelette grating, is highly efficient in the diffraction of wavelengths close to those for which specular reflection occurs. The wavelength at which specular reflection and first-order diffraction coincide is called the blaze wavelength, λ_B. Energy is concentrated in the first order at λ_B, at half λ_B in the second order, and so on.

There are other types of special gratings. An **echelle grating** is ruled with step-shaped rulings a few hundred times wider than the average wavelength to be studied. This is in contrast to the general arrangement where the line spacing is similar to the average wavelength. The echelle is used, however, at orders, n, of 100 or more and is thus capable of **considerable dispersion**. The manufacture of precision gratings is very demanding and **replica** gratings are **cast** in plastic from an original.

A grating may be mounted in a monochromator in several ways. One method uses the **Littrow** mounting, shown in Fig. 1.3. Another arrangement, the **Ebert** mounting (Fig. 1.5), uses a large spherical mirror to collimate and focus the beam. **Czerny and Turner** suggested replacing the large,

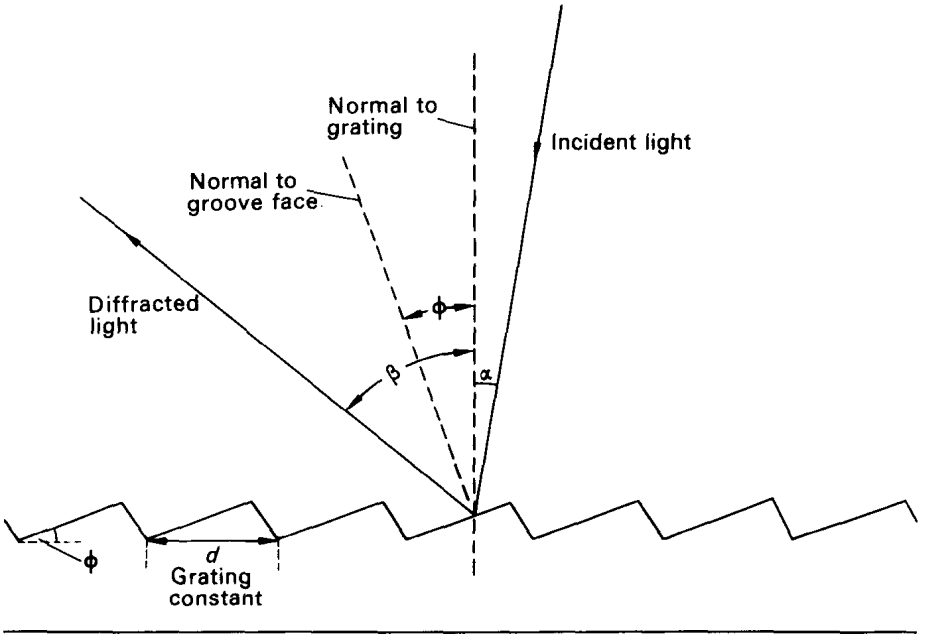


Fig. 1.4 Schematic diagram of a blazed reflection grating.

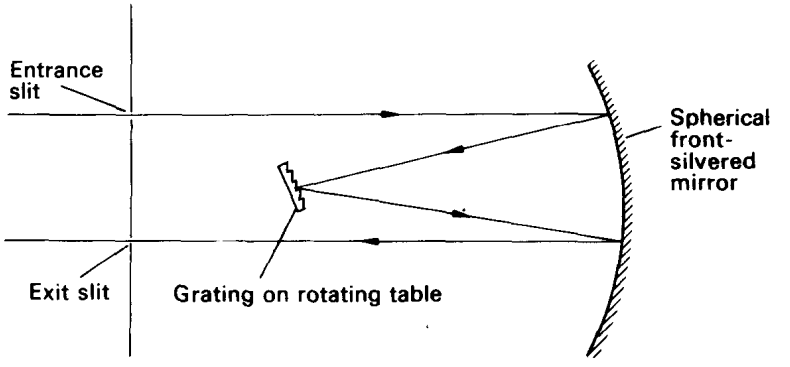


Fig. 1.5 Ebert mounting for a reflection grating.

expensive Ebert mirror with two small, spherical mirrors mounted symmetrically, as shown in Fig. 1.6. The Czerny–Turner mounting is very popular for atomic absorption spectrometers as it combines economy with relative freedom from aberrations.

此为试读,需要完整PDF请访问: www.ertongbook.com